Structural Ordering in Nanotube Polymer Composites

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The structure properties in carbon nanotube (CNT) polymer composite interface has been studied through molecular dynamics simulations. Polymer (polyethylene) molecules are found to form discrete adsorption layers as a function of radial distance from the axis of the nanotube. The molecules within the adsorption layers prefer to align parallel to the tube axis. A structural order parameter of orientation, S_Z, has been investigated in detail, and shows a discrete peaking behavior that is in correlation with the peaks in the density distribution function. An increase in the structural order parameter has been shown to contribute towards the mechanical modulus of the composite, and the orientation related changes have been found to be inelastic in nature.

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Since their discovery in 1991 Carbon nanotubes (CNTs) [1] have been found to have good mechanical properties with high Young's modulus, and unique structure dependent electronic properties. Using CNTs as nanofibers has been pursued extensively both in experimental and theoretical studies to enhance the mechanical [2–7], electronic [8–10], thermal [11, 12], and optical [13] properties of the composite materials. The advantages of CNTs as nanofibers include their light weight, high aspect ratio, and large surface area, which are good for physical absorptions or chemical bonding. One of the widely investigated matrix materials is polymers in CNT based nanocomposites. Studies have shown that the additions of only small fractions of CNTs can significantly change the properties of polymer materials [8–10]. The atomic scale structures of CNT composites, especially the relative structures at the polymer matrix and CNT interface, are expected to explain many unique properties found in the nanotube nanocomposites.

We use molecular dynamics (MD) simulation (DLPOLY package [14]) to study the structural ordering and the related mechanical properties of polymer CNT composites. Discrete adsorption layers of polyethylene molecules have been observed to form around CNT fibers. We find that the orientations of the surrounding polymer molecules prefer to align parallel to the embedded CNT axis, and that such alignment is maximized in the adsorption layers. A structural order parameter S_Z has been defined and investigated, in which an increase in S_Z is found to contribute towards the enhancement of the Young's modulus of the nanocomposite.

The polyethylene (PE) is chosen as a matrix in the study, due to its simplicity and generic representation feature for polymeric materials. In each periodic unit cell ($\sim 30\text{Å} \times 30\text{Å} \times 30\text{Å}$) a capped CNT (10, 0) is embedded for the simulations of the CNT composite. The Tersoff-Brenner potential [15, 16] is used for C-C interactions for carbon atoms in the CNT. The PE molecule chains are flexible and are treated within a united-atom model, where the vibrations of C-C bonds, dihedral, and torsional interactions are allowed. The interfacial interaction between the CNT and the PE matrix is through a 6-12 type Lennard-Jones van der Waals (VDW) potential. The nanocomposite is prepared at relatively high temperature in liquid state, and then cooled down to low temperatures into glassy solid state. The details of the force field and sample preparation process are described elsewhere [11].

A composite system of 80 PE molecules with 10 repeating units in each chain, and a $\sim 20\text{Å}$ long capped (10, 0) CNT, is prepared at 300K and then cooled down to 50K. The cooling rate is 1K/1ps with the pressure kept constant at 1bar. The volume fraction of CNT in the composite is about 8%. We focus on the structure of the system in glassy state with T = 50K because the applications of CNT composites are mainly in the solid state region. The radical distribution function (RDF) $g(r)$ for the PE molecules around the embedded CNT as a function of the radical distance r from the axis of the nanotube, is shown in Figure 1a. The RDF is for the distribution in the XY plane perpendicular to the tube axis along the Z direction (see the insert of Fig. 1a for the definition of the coordinates). The r is expressed in unit of r^*, where $r^* \sim 3.5\text{Å}$ is the VDW equilibrium distance between C atoms. The data is averaged from 6 sample sets and the corresponding error bars are also marked in the figure. The RDF function of the PE molecules around the CNT fiber shows discrete peaks at $r \sim 2.3r^*$ and $3.5r^*$, which represent the formation of discrete adsorption layers in the surrounding molecules. The largest density is found in the first layer and decreases with increasing r. A combined atomic configuration (top view) of the composite, representing over 6 sample sets, is

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shown in Fig. 1b, where the embedded CNT is at the center. Two rings of dense polymer molecules can be observed, showing the two discrete adsorption layers directly. As the radius of the (10, 0) CNT is about 3.9Å, the mean distance of the PE molecules in the two layers from the CNT wall is about 4.15Å and 8.35Å. Limited by the size (30Å × 30Å in the plane perpendicular to the tube axis) of the simulation cell, the function $g(r)$ is shown only up to $r \sim 4.5r^*$. Similar discrete peaks with decreasing amplitudes in the density of polymer molecules have also been observed near solid surfaces, and have been suggested to affect the dynamics and rheology of polymer molecules [17, 18]. The observed small value of $g(r)$ for $r/r^* < 1$ is due to the small space available for the polymer molecules in between the adjoining CNT fibers along the Z axis, for the system in the study.

The structures of the PE molecules around the CNT are further investigated through an orientation order parameter. The local orientation of a PE molecule backbone can be described through the orientation of the vector connecting the two ends of a subchain, and in the analysis we consider subchains with 4 segments on the same molecule. The orientation order parameter for the PE molecules along the CNT axis, Z, is thus defined as $S_Z(r) = 0.5(3\langle \cos^2 \theta(r) \rangle - 1)$ [19], where θ is the angle between the vector and the CNT axis with the center mass of the subchain at a distance r from the CNT axis, in the XY plane. The S_Z as a function of r/r^* is plotted in Figure 2. It can be seen that the orientation order parameter S_Z has maximum values at $r \sim 2.3r^*$ and $3.5r^*$, which are at the same locations of the two adsorption layers of PE molecules shown in Fig. 1a. This suggests that the polymer molecules distributed in the discrete adsorption layers not only have higher density but also have a more ordered structure with the orientation of the backbones aligned parallel to the CNT axis. Such an alignment is expected to affect the mechanical response of the CNT composites, and is discussed below. The negative value of $S_Z(r)$ in the region $r/r^* < 1$ is also due to the limited space in between two adjoining CNT fibers in the Z direction. The polymer molecules prefer orientations in the XY plane in this region (for example near the top and bottom of the simulation cell shown in the insert of Fig. 1a.).

The mechanical properties and the Young's modulus of the solid PE-CNT composite at T = 50K is studied through a direct calculation of the stress-strain response from the MD simulations. A tensile stress is applied to the CNT composite gradually at a rate of 1bar/1ps. The anisotropic Berendsen NPT ensemble [20, 21] is used, in which the size and shape of the unit cell is coupled to the external applied stress; and the responding internal stress and strain can then be obtained. The loading direction is kept parallel to the nanotube axis. The Young's modulus of the CNT composites, calculated from the small strain region, is found to be around 1970 ± 248 MPa, which is about 30% larger than that of the pure PE bulk system at 1493 ± 100 MPa. Both of the values were averaged from data of 6 sample sets. A large tensile strain was applied up to and beyond the failure point of the composite. The composite and pure PE system yield at a similar strain around 10%, while the tensile strength of the former (~ 1 KPa) is about 20% larger than the pure PE system (~ 0.8 KPa). The Young's modulus of the CNT composites is well below the upper bound expected from the linear mixing rule, $Y_{comp} = V_{fiber}Y_{fiber} + V_{matrix}Y_{matrix}$, where the subscript "$comp$" is for composite systems, and V and Y are the corresponding volume ratio and the Young's modulus, respectively. This is because the linear mixing rule is valid only for continuous fibers with perfect bonding between polymer matrix and fibers. The CNT fibers in our simulations and in most experiments are discontinuous, in which cases the aspect ratio of the fibers will play a significant role. The calculated Young's modulus is above the lower bound of about 1600 MPa as according to $1/Y_{comp} = V_{fiber}/Y_{fiber} + V_{matrix}/Y_{matrix}$ predicted from the variational theory [22].

The intermolecular VDW interaction is found to contribute most towards the mechanical response of the CNT composites to the applied tensile strain. The intramolecular C-C bond vibrations, bond bending and torsion are less important. Only a small load transfer between the PE molecules and the CNT is found by observing the change of the C-C bond length on the CNT, and such a load transfer is found to occur only within 1% tensile strain for the system studied here. The low load transfer is not surprising since only weak VDW interactions are included between the matrix and the CNT fibers. The chemical bonding between the CNT and the matrix molecules has been found to increase the load transfer [23, 24]. The short length of the CNT due to the simulation cell size limitation is also not helpful for large load transfers. We attribute the enhanced modulus of the CNT composite to the structural factors. The well oriented and densely layered structures of PE molecules in the CNT composite are expected to increase the VDW interactions between the PE molecules themselves and with the embedded CNT fiber. This can lead to a better load transfer between the nanotube fiber and polymer matrix.

At the yielding point of the polymeric material, plastic deformations appear with permanent structural changes. Detailed analysis shows that the orientation ordering of the PE molecules plays an important role in the plastic deformation in the composite. With the applied tensile strain, the PE molecules tend to align with the loading direction (same as the CNT axis). The total orientation order parameter $S_Z = \int S_Z(r)dr$ increases with the applied tensile strain, as shown in Figure 3. After applying a 1 KPa tensile stress to the CNT composite up to 10% strain, the stress was gradually removed. A permanent change of the shape of the composite is found with a residue strain of about 5%, indicating that a plastic deformation has happened in the stressed nanocomposite material. The orientation order parameter S_Z, in this case, is found not fully recovered to its initial value but rather to a higher value. This suggests that the structural changes in the polymer matrix and the orientation ordering of the molecules in the

surrounding layers are not fully elastic.

As described above, the structural orderings in the CNT nanocomposites have strong influence on the mechanical properties of the materials. The orientation alignment of the polymer molecules along the CNT axis can enhance the diffusions of the molecules, especially along the tube axis, which has been found in previous MD simulation studies [11]. Larger systems with longer nanotubes and polymer molecules could conceivably have larger structural ordering effects because the large surface area and the relative interactions at a longer length scale could induce stronger collective structural arrangements. Premilary studies on a larger system, consisting of 200 Å long CNTs and 100-unit PE molecules, have shown that the peaks (in the RDF) of the adsorption layers of the polymer molecules around the nanotube have higher magnitudes compared with the peaks in the smaller size system described in this work. The observed peaks also broaden with increasing temperatures. A drop in the value of the orientation order parameter S_Z for temperatures above the glass transition is observed. This indicates that the structural ordering of the polymer molecules may play an important role in the molecule conformation frozen during the glass transition process. Studies on these issues are currently underway and will be published elsewhere.

In summary, we have used MD simulations to study the structural ordering and the mechanical properties of polyethylene CNT composites. The polymer molecules are found to form discrete adsorption layers with peaks in the RDF. The alignment of the molecules with the nanotube axis within the adsorption layers is also found. The increased orientation ordering leads to an enhancement of the mechanical modulus of the nanocomposite materials, and such structural ordering also plays an important role in the yielding behavior of the materials. It is also expected that the structural ordering of the polymer molecules could significantly influence thermal and electrical transport, as well as optical behavior of carbon nanotube composite materials. While the chirality of CNTs is expected to have minor effects on the structural ordering and mechanical properties of the polymer composites discussed in this letter, it could be much different cases for electronic or optical properties. Metallic and semiconducting CNTs are expected to behave differently regarding the changes of their band structures with the presence of polymer matrix molecules; and thus could affect the overall electronic/optical properties of the nanocomposites in different ways.

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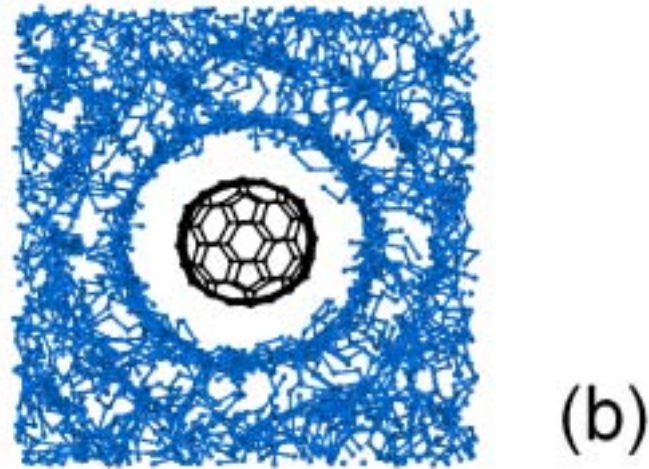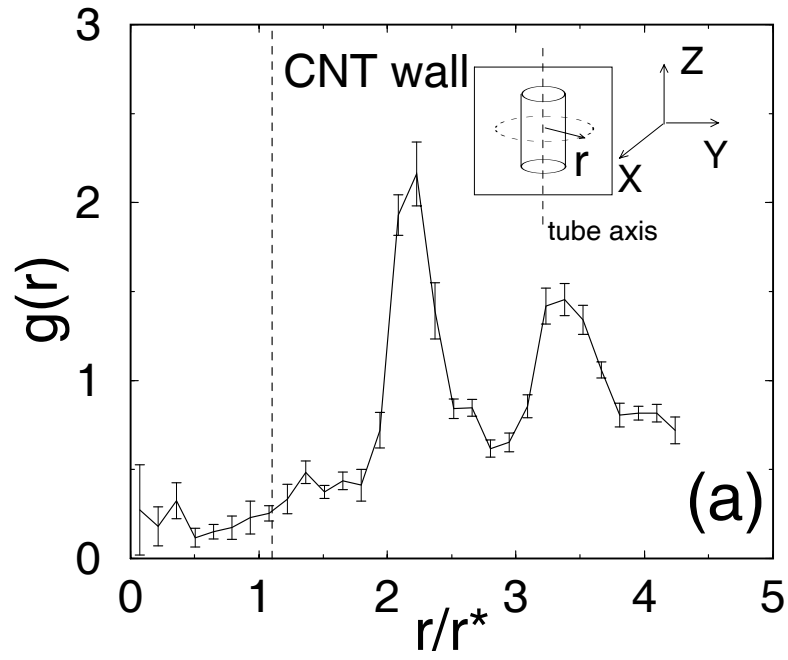[24] S.J.V. Frankland, A. Caglar, D.W. Brenner, and M. Griebel, J. Phys. Chem. B **106**, 3046 (2002).

FIG. 1: (a) The radical distribution function g(r) of the polyethylene (PE) molecules around the CNT as a function of the distance from the axis of the tube in the XY plane (averaged from 6 sample sets, with error bars marked). Insert: a schematic plot of the unit cell of the CNT composite in the simulation and the definition of the coordinates the system used. The polymer molecules are not shown. (b) Top view of the combined atomic configuration of 6 sample sets of CNT (black color) PE (blue color) composite in ball-and-stick plot. The polymer molecules above the CNT along the axis direction are not shown for clarification.
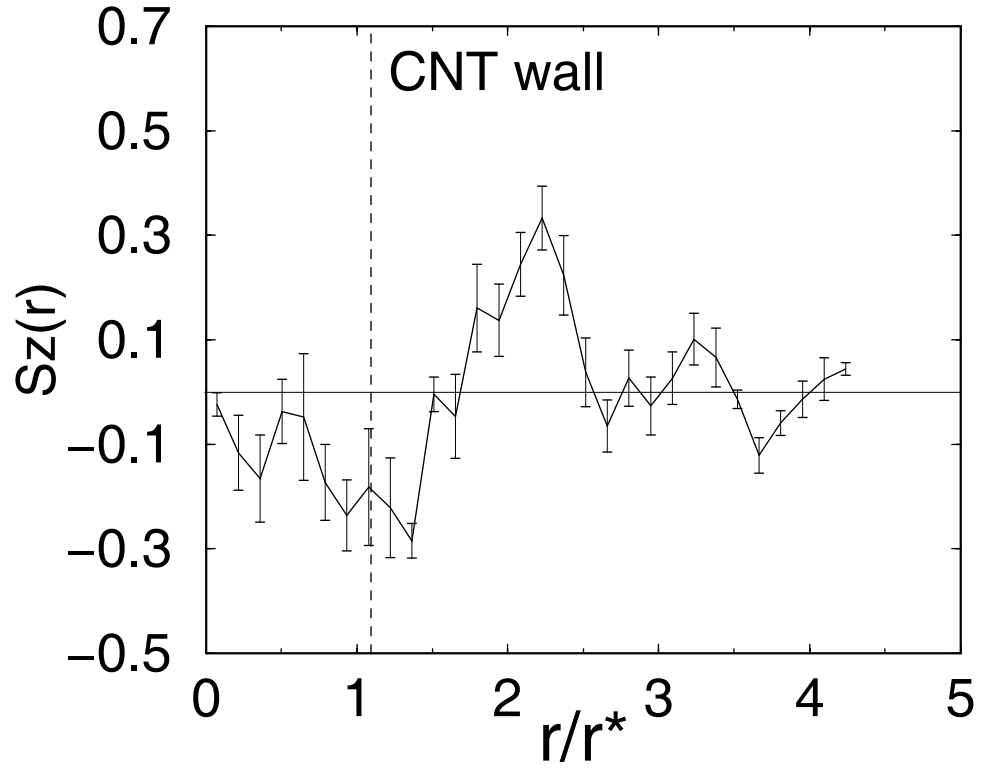
FIG. 2: The orientation order parameter as a function of the distance from the CNT axis in the XY plane for the polymer molecules in the composites (averaged from 6 sample sets, with error bars marked). See Fig. 1 for the definitions of the coordinates XYZ.
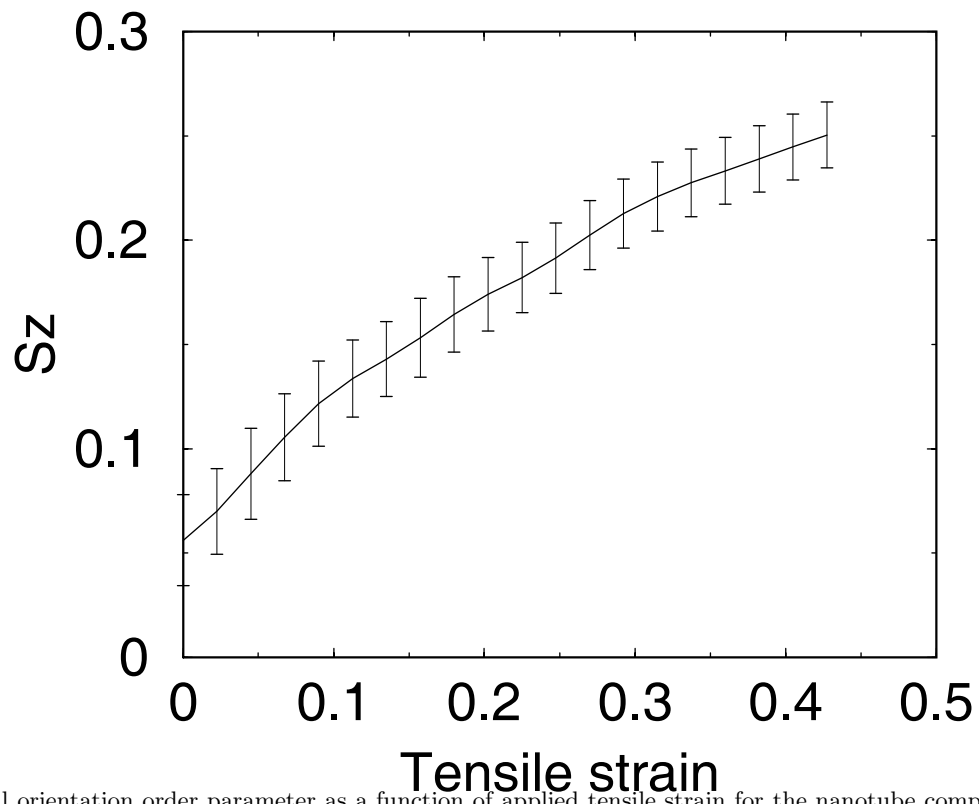
FIG. 3: The total orientation order parameter as a function of applied tensile strain for the nanotube composites.The data is averaged from 6 sample sets, with error bars marked.